

# Diurnal Variation in Rates of Calcification and Carbonate Sediment Dissolution in Florida Bay

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**ABSTRACT:** Water quality and circulation in Florida Bay (a shallow, subtropical estuary in south Florida) are highly dependent upon the development and evolution of carbonate mud banks distributed throughout the Bay. Predicting the effect of natural and anthropogenic perturbations on carbonate sedimentation requires an understanding of annual, seasonal, and daily variations in the biogenic and inorganic processes affecting carbonate sediment precipitation and dissolution. In this study, net calcification rates were measured over diurnal cycles on 27 d during summer and winter from 1999 to 2003 on mud banks and four representative substrate types located within basins between mud banks. Substrate types that were measured in basins include seagrass beds of sparse and intermediate density *Thalassia* sp., mud bottom, and hard bottom communities. Changes in total alkalinity were used as a proxy for calcification and dissolution. On 22 d (81%), diurnal variation in rates of net calcification was observed. The highest rates of net carbonate sediment production (or lowest rates of net dissolution) generally occurred during daylight hours and ranged from 2.900 to  $-0.410 \text{ g CaCO}_3 \text{ m}^{-2} \text{ d}^{-1}$ . The lowest rates of carbonate sediment production (or net sediment dissolution) occurred at night and ranged from 0.210 to  $-1.900 \text{ g CaCO}_3 \text{ m}^{-2} \text{ night}^{-1}$ . During typical diurnal cycles, dissolution during the night consumed an average of 29% of sediment produced during the day on banks and 68% of sediment produced during the day in basins. Net sediment dissolution also occurred during daylight, but only when there was total cloud cover, high turbidity, or hypersalinity. Diurnal variation in calcification and dissolution in surface waters and surface sediments of Florida Bay is linked to cycling of carbon dioxide through photosynthesis and respiration. Estimation of long-term sediment accumulation rates from diurnal rates of carbonate sediment production measured in this study indicates an overall average accumulation rate for Florida Bay of  $8.7 \text{ cm } 1000 \text{ yr}^{-1}$  and suggests that sediment dissolution plays a more important role than sediment transport in loss of sediment from Florida Bay.

## Introduction

The production and deposition of biogenic carbonate sediments plays a key role in the development of the topographic structure and chemical and biological characteristics of many coastal ecosystems. Production of carbonate sediments and skeletal material in coral reef ecosystems provides the topographic relief that supports biological diversity (Friedlander and Parrish 1998), enables reefs to keep up with rising sea level (Smith and Kinsey 1976), and protects the coastline from erosion (Cesar and van Beukering 2004). While the coastal ocean covers only 7% of the surface of the global ocean, it accounts for 90% of sedimentary remineralization and 50% of the deposition of calcium carbonate sediments (Gattuso et al. 1998).

Rates of biogenic carbonate sediment production are affected by natural and anthropogenic alterations in water quality parameters including temperature, salinity, nutrients, light availability,  $\text{pCO}_2$ , and aragonite saturation state (Barnes and Chalker 1990; Kleypas et al. 1999; Leclercq et al. 2002). Identifying potential changes in sediment production resulting from perturbations in these water

quality parameters is essential for predicting the effects of resource management actions on the health of coastal ecosystems. While anthropogenic effects on natural systems may continue to change and remain apparent for very long periods of time (hundreds to thousands of years), initial ecosystem responses to anthropogenic alteration typically occur on very short time scales (a few months to a few years; McIvor et al. 1994). It is critical to understand both short-term and long-term variability of sediment production to accurately predict ecosystem responses. The aim of this study was to measure diurnal fluctuations in rates of calcification and dissolution in Florida Bay (a shallow, subtropical estuary located along the south coast of the Florida peninsula, Fig. 1) to identify short-term variability in sediment production that may affect long-term rates of carbonate sediment production (measured over yearly time scales) and accumulation (over thousands of years).

The production and transport of biogenic carbonate sediments in Florida Bay is responsible for the development of mud banks that alter circulation patterns, surface water chemistry, and the distribution of benthic habitats. Accurate measurements of sediment accumulation and production rates are required to determine how these processes have

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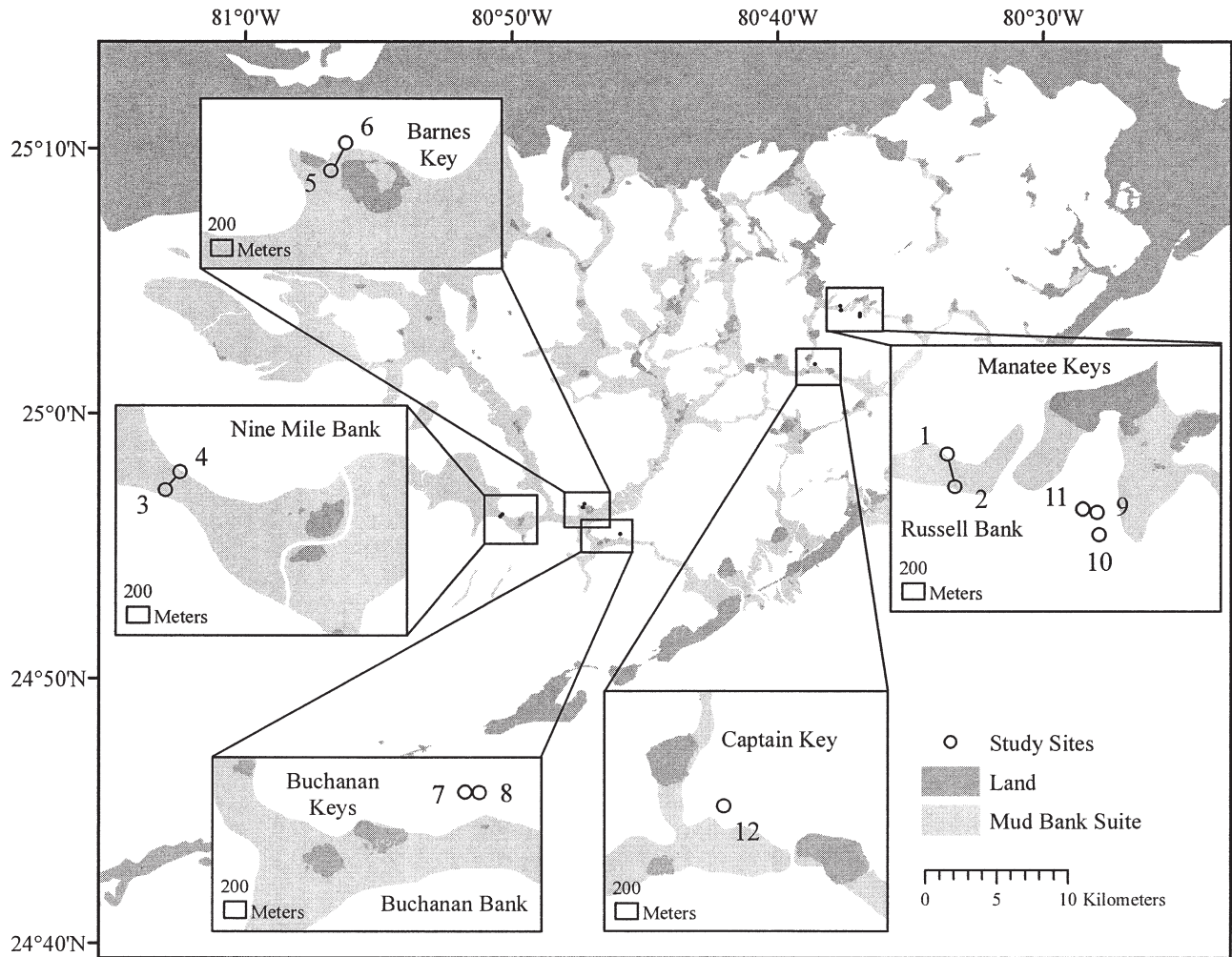


Fig. 1. Locations of mud bank and basin study sites in Florida Bay. Open circles indicate basin sites. Open circles connected by lines indicate the beginning and end of mud bank transects. Numbers correspond to numbered locations in Table 1.

changed during the last century and to predict how they may change in the future in response to large-scale restoration activities in south Florida that will change the flow and quality of freshwater entering Florida Bay (Fourqurean and Robblee 1999; U.S. Army Corps of Engineers 1999). Estimates of both long-term sediment accumulation rates ( $\text{cm } 1000 \text{ yr}^{-1}$ ) and annual carbonate sediment production rates based on standing crop and growth rates of various calcifying species are available for Florida Bay from previous research (Stockman et al. 1967; Nelson and Ginsburg 1986; Bosence 1989a; Frankovich and Zieman 1994), but discrepancies occur, not only between long-term accumulation rates and short-term productivity measurements, but also among short-term productivity measurements.

Estimates of annual biogenic carbonate sediment production range from  $1.9\text{--}238 \text{ g CaCO}_3 \text{ m}^{-2} \text{ yr}^{-1}$

(Frankovich and Zieman 1994) to  $448\text{--}1,042 \text{ g CaCO}_3 \text{ m}^{-2} \text{ yr}^{-1}$  (Bosence 1989a). Annual rates of sediment production overestimate long-term rates (thousands of years) of sediment accumulation (Stockman et al. 1967). Differences among annual (short-term) productivity rates determined by standing crop methods have been attributed to variations in methodology, annual changes in seagrass leaf productivity, and the calcifying organisms included in or excluded from studies (Frankovich and Zieman 1994). Standing crop methods for measuring short-term carbonate sediment production account for gross sediment production and do not include the effects of sediment transport or dissolution. Long-term sediment accumulation rates based on sediment thickness account for sediment production, dissolution, and transport. Differences between short-term productivity measurements and long-term accumulation measurements have been

attributed primarily to transport of sediment both within and out of Florida Bay (Stockman et al. 1967; Bosence et al. 1985; Bosence 1989a,b; Prager and Halley 1999). Sediment dissolution in pore waters has also been identified as a potential mechanism for loss of sediment in Florida Bay. Very few studies have attempted to quantify porewater dissolution (but see Walter and Burton 1990; Rude and Aller 1991; Walter et al. 1993; Ku et al. 1999). Despite these differences, most investigators agree that the highest production rates are observed in western Florida Bay and are associated with mud banks as opposed to basins (Stockman et al. 1967; Ginsburg 1979; Nelson and Ginsburg 1986; Bosence 1989a).

While long-term and annual carbonate sediment production in Florida Bay are quite well known, seasonal and diurnal variability remain largely unstudied despite the fact that the calcifying organisms responsible for most of the biogenic sediment production in Florida Bay respond to daily and seasonal environmental changes. We have measured short-term, net carbonate sediment production in Florida Bay to examine diurnal and seasonal variability using the alkalinity anomaly technique (Broecker and Takahashi 1966; Smith and Key 1975), which has proven successful for measuring production in carbonate reef and seagrass bed ecosystems (Smith and Key 1975; Chisholm and Gattuso 1991; Gattuso et al. 1993, 1997; Boucher et al. 1998). We define net carbonate sediment production as gross sediment production minus sediment dissolution. The alkalinity anomaly method provides an independent measure of net sediment production that incorporates biogenic calcification by all carbonate-producing species, nonbiogenic calcification, and sediment dissolution.

#### STUDY AREA

Florida Bay is a subtropical estuary characterized by numerous mangrove islands that are connected by submerged, shallow mud banks that bound basins averaging 2 m in water depth (Fig. 1). The western zone of Florida Bay is open to the Gulf of Mexico and is tidally influenced with relatively stable marine conditions. Circulation in central Florida Bay is restricted by mud banks with little tidal influence and is controlled primarily by wind-driven currents (Fourqurean and Robblee 1999). Salinity in the central zone is variable and frequently exhibits hypersalinity during summer months due to increased evaporation rates and long water residence times (Fourqurean et al. 1993). Water temperature throughout the Bay has a median value of approximately 26°C and shows distinct seasonal signals ranging from a high of approximately 30°C during summer months to a low of 20°C during

winter months (Boyer et al. 1999). Dissolved organic matter and N:P ratios are typically higher in the central zone than in the western zone. Banks are comprised of biogenic carbonate mud derived primarily from calcareous green algae, a variety of seagrass epiphytes, mollusks, and stony corals (Stockman et al. 1967; Nelson and Ginsburg 1986; Bosence 1989a; Frankovich and Zieman 1994). Wanless and Tagett (1989) subdivided the Bay into western, central, and eastern zones characterized by different mud bank processes. Western Florida Bay is considered a zone of mud bank formation where mud banks are accreting fast enough to keep pace with sea level rise. Central Florida Bay is a zone where mud banks migrate, erosion and deposition appear to be in equilibrium, and mud banks move as sediments are eroded from one side and deposited on the other. Seagrass communities covering much of Florida Bay consist primarily of *Thalassia testudinum*, *Halodule wrightii*, and *Syringodium filiforme*, with *Thalassia* being the most abundant.

#### Methods

Study sites for monitoring of carbonate sediment production were established on a mud bank named Russell Bank and in basins near Manatee Keys and Captain Key in central Florida Bay. Study sites in western Florida Bay included mud banks named Nine Mile Bank and Barnes Key Bank and a basin located near Buchanan Keys (Fig. 1 and Table 1). Russell Bank and Nine Mile Bank monitoring sites were located on mud banks where sediment cores were previously taken (Brewster-Wingard and Ishman 1999; Halley and Roulier 1999; Robbins et al. 2000) or where permanent sediment elevation tables were installed in transects across the bank to measure long-term sediment accumulation rates and bank migration (Halley et al. 2001). Elevation profiles for the Nine Mile Bank and Russell Bank study sites are available from Halley et al. (2001). No elevation profiles are available for Barnes Key Bank. Monitoring sites located in basins near Buchanan Keys, Captain Key, and Manatee Keys were located in areas where previous sediment production studies have been conducted (Stockman et al. 1967; Nelson and Ginsburg 1986; Bosence 1989a; Walter and Burton 1990; Ku et al. 1999).

Four representative bottom types were chosen for monitoring in basins to reflect bottom-type categories previously mapped by Prager and Halley (1999). These representative bottom types included sparse and intermediate density *Thalassia* communities and mud bottom and hard bottom communities (Prager and Halley 1999). Dense seagrass beds were located on the tops of mud bank sites including Russell, Nine Mile, and Barnes Key Banks.



TABLE 1. Study site locations and descriptions.

Location	Description	Latitude	Longitude	Water depth (m)
1. Russell Bank	Mud bank transect beginning	25°04.034'N	80°37.669'W	0.60
2. Russell Bank	Mud bank transect end	25°03.872'N	80°37.631'W	0.60
3. Nine Mile Bank	Mud bank transect beginning	24°56.071'N	80°50.436'W	0.60
4. Nine Mile Bank	Mud bank transect end	24°56.160'N	80°50.366'W	0.60
5. Barnes Key Bank	Mud bank transect beginning	24°56.404'N	80°47.340'W	0.62
6. Barnes Key Bank	Mud bank transect end	24°56.542'N	80°47.268'W	0.62
7. Basin near Buchanan Keys	Intermediate <i>Thalassia</i> bed	24°55.415'N	80°45.948'W	1.52
8. Basin near Buchanan Keys	Hard bottom community	24°55.407'N	80°45.939'W	1.52
9. Basin near Manatee Keys	Intermediate <i>Thalassia</i> bed	25°03.745'N	80°36.931'W	1.50
10. Basin near Manatee Keys	Mud bottom	25°03.636'N	80°36.921'W	1.50
11. Basin near Manatee Keys	Sparse <i>Thalassia</i> bed	25°03.748'N	80°36.933'W	1.50
12. Basin near Captain Key	Sparse <i>Thalassia</i> bed	25°01.838'N	80°38.602'W	1.37

Hard bottom communities located in the basin near Buchanan Keys were characterized by small, sparsely distributed corals (*Porites* sp. and *Siderastrea* sp.), sponges, octocorals, and calcareous and fleshy macroalgae.

Rates of net carbonate sediment production (calcification) were measured over 24-h time periods during winter (March) and summer (July–September) at each study location from March 1999 to March 2003. Rates of calcification were determined from precise measurements of total alkalinity (TA) using the alkalinity anomaly technique described by Smith and Key (1975) whereby calcification is equivalent to half of the change in TA measured over time or spatially along sampling transects. Prior to February 2002, TA was measured using the automated Gran titration method, equations, and automated titration system described in Millero et al. (1993). The automated titration system consisted of a plexiglas water-jacketed, fixed volume (200 ml) sample cell from the laboratory of Dr. Frank Millero (University of Miami, Rosenstiel School of Marine and Atmospheric Science), a Metrohm 665 Dosimat titrator, an Orion 720A pH meter, an Orion Ross glass pH electrode, and Orion double-junction Ag/AgCl reference electrode interfaced with a personal computer. The temperature of both the acid titrant and the sample cell were controlled to a constant value of  $25 \pm 0.05^\circ\text{C}$  with a Lauda RE106 thermostated water bath. Standardized hydrogen chloride (HCl) used for titrations and standardized reference material (SRMs) used to determine the reliability of alkalinity measurements were provided by Dr. Millero. TA was calculated from the acid concentration, cell volume, salinity, temperature, measured emf, and volume of HCl using an automated titration program. SRMs and triplicates of samples were measured approximately once every ten samples to determine accuracy and precision of our titration system. Measurement of 34 SRMs yielded an accuracy of  $0.003 \text{ mmol kg}^{-1}$ . Triplicate sample

analyses ( $n = 31$ ) yielded an average precision of  $0.001 \text{ mmol kg}^{-1}$ . A correction factor was determined from the measured and reported SRM values and used to correct all TA measurements.

TA samples collected after February 2002 were measured using spectrophotometric techniques described by Yao and Byrne (1998). Absorbance measurements were made using an Ocean Optics USB2000 spectrometer and Ocean Optics software package OOIBase 32. Both water sample amount (approximately 130 g) and acid additions were determined gravimetrically using a Denver Instruments PI-214 analytical balance ( $\pm 0.1 \text{ mg}$ ). Water samples were placed in preweighed glass cells (Hellma Cells, Inc. Plainview, New York) and weighed again to determine exact sample weight by difference. Baseline absorbance was measured before adding bromocresol purple indicator (0.004 M) to each sample. Titrations were performed by addition of 0.100 N standardized HCl ( $\pm 0.0001 \text{ N}$ ) from a plastic syringe fitted with a Teflon syringe needle. The pH was measured continuously throughout the titration to an end point of approximately 4.3, and the weight of the acid was determined by difference in syringe weight before and after acid addition. At the end of each titration, the solution was purged with a stream of  $\text{N}_2$  gas presaturated with  $\text{H}_2\text{O}$ . After purging, final absorbance measurements were made, and solution temperature was determined using a Hart Scientific 1521 ( $\pm 0.1^\circ\text{C}$ ) handheld thermometer. TA was calculated using the equations of Yao and Byrne (1998). Accuracy of our spectrophotometric alkalinity measurements was determined by comparison to certified reference material (CRM) from the laboratory of Dr. Andrew Dickson (Scripps Institute of Oceanography; see Dickson et al. 2003). CRMs and duplicates of samples were measured approximately once every ten samples to determine accuracy and precision of our titration system. Measurement of five CRMs yielded an accuracy of  $0.004 \text{ mmol kg}^{-1}$ . Duplicate sample analyses ( $n =$

6) yielded an average precision of  $0.001 \text{ mmol kg}^{-1}$ . A correction factor was determined from the measured and reported CRM values and used to correct all TA measurements. Based on the alkalinity anomaly theory (Smith and Key 1975), precipitation of  $1 \text{ mg kg}^{-1}$  seawater of  $\text{CaCO}_3$  causes a change in TA of  $0.020 \text{ mmol kg}^{-1}$  seawater. We report calcification rates calculated from our TA measurements to the nearest  $1 \text{ mg}$ , which is well above detection limits based on our precision and accuracy.

Temperature, conductivity, pH, and dissolved oxygen (DO) were also measured continuously during monitoring expeditions using an Orion Ross pH electrode ( $\pm 0.005 \text{ pH unit}$ ), salinity ( $\pm 0.1 \text{ psu}$ ) and temperature ( $\pm 0.1^\circ\text{C}$ ) probes, and a YSI DO meter and pressure-compensated field probe ( $\pm 0.01 \text{ mg L}^{-1}$ ). pH electrodes were calibrated using Tris seawater buffers prepared at an ionic strength of 0.7 and scaled to free hydrogen ion concentration scale (Millero 1996).

Calcification at mud bank study sites was determined using a flow-respirometry sampling strategy to measure spatial chemical changes across the banks (Smith 1973; Marsh and Smith 1978). Sampling sites were located upstream and downstream from 200 to 400 m transects across Russell Bank, Nine Mile Bank, and Barnes Key Bank. Mud banks usually have extremely level and uniform tops with sloping flanks (Halley et al. 2001). Upstream and downstream sampling sites were located at the edges of bank tops above the sloping flanks to minimize variation in bathymetry along transects. Measurements on Russell Bank were taken during March and September of 1999 and 2000. Measurements were performed during October 1998 and March 1999 on Nine Mile Bank and July 2000 on Barnes Key Bank. Water samples were collected and analyzed for TA at upstream and downstream sites approximately every 4 h throughout 24-h time intervals. In situ pH, temperature, and DO were measured at the time of water sample collection. Current directions and velocities were determined by deploying Sontek Acoustic Doppler Velocimeters on the bank tops near upstream or downstream sampling sites located near the flanks of banks. Calcification rates were determined from TA, current velocity, and sample-transect length, width, and depth. The change in TA ( $\text{mol m}^{-3}$ ) was determined by difference in concentration between upstream and downstream sampling stations. The volume of water transported along a transect per unit time ( $\text{m}^3 \text{ 4 h}^{-1}$ ) was calculated from the current velocity and length, width, and depth of each sample transect (assuming a transect width of 1 m). Transect lengths were determined from latitude and longitude of upstream and downstream

sample locations. Transect area ( $\text{m}^2$ ) was determined from its length and an assumed width of 1 m. Rates of calcification,  $C$  ( $\text{g CaCO}_3 \text{ m}^{-2} \text{ 4 h}^{-1}$ ), were calculated as half the change in TA ( $\text{mol m}^{-3}$ ) times the volume of water transported along a transect per unit time,  $V$  ( $\text{m}^3 \text{ 4 h}^{-1}$ ), divided by the area of a transect,  $A$  ( $\text{m}^2$ ), times the molecular weight of  $\text{CaCO}_3$ , MW ( $100.09 \text{ g mol}^{-1}$ ):  $C = \frac{1}{2}\Delta\text{TA} \times V/A \times \text{MW}$  (Smith 1973; Smith and Key 1975; Barnes and Devereux 1984).

Calcification rates were determined in basins by measuring TA changes in a large incubation chamber (surface area of  $11 \text{ m}^2$ ), called the Submersible Habitat for Analyzing Reef Quality (SHARQ, U.S. Patent #6,467,424 B1), deployed on representative bottom type communities using methods previously described by Yates and Halley (2003). Bottom types included intermediate *Thalassia* beds adjacent to hard bottom communities located near Buchanan Keys, intermediate *Thalassia* beds adjacent to mud bottoms near Manatee Keys, and sparse seagrass beds near Captain Key and Manatee Keys. Intermediate seagrass beds were measured during March and September 1999 and 2000. Hard bottom sites were measured during March 2000. Mud bottom sites were measured during March and September 2000 and March 2003, and sparse seagrass beds were measured during March 2001 and March 2003. Salinity, temperature, pH, and DO were measured continuously through the incubation chamber's flow-through analytical system throughout the duration of incubation periods (20–28 h). Fluorescein dye was injected into the incubation chamber during each deployment to determine incubation chamber volume, mixing rate, and leakage as described previously by Yates and Halley (2003). Water samples were removed from incubation chamber sample ports every 4 h for TA measurements. TA of ambient water (i.e., located outside of the incubation chamber) was measured every 4 h during 8 of 21 incubation chamber deployments. Rates of net calcification ( $C$ ) were calculated for each 4-h interval between alkalinity measurements during chamber incubation periods using the equation  $C$  ( $\text{g CaCO}_3 \text{ m}^{-2} \text{ 4 h}^{-1}$ ) =  $\frac{1}{2}\Delta\text{TA}$  ( $\text{mol m}^{-3} \text{ 4 h}^{-1}$ )  $\times$  SHARQ volume ( $\text{m}^3$ )/SHARQ surface area ( $\text{m}^2$ )  $\times$  MW ( $\text{g mol}^{-1}$ ).

Net daytime carbonate sediment production rates ( $C_{\text{day}}$ ,  $\text{g CaCO}_3 \text{ m}^{-2} \text{ d}^{-1}$ ) were calculated for both banks and basins by integrating calcification rate curves with respect to net calcification rates determined every 4 h throughout incubation periods from sunrise to sunset. Sediment production rates for 24 h ( $C_{\text{net}}$ ,  $\text{g CaCO}_3 \text{ m}^{-2} \text{ 24 h}^{-1}$ ) were calculated by integrating each data set over the entire diurnal cycle. A y-axis reference point of zero was used in all

TABLE 2. Net calcification rates of mud banks in Florida Bay.

Substrate description	Date	Total alkalinity (mmol kg <sup>-1</sup> )		Hours of sunlight	C <sub>day</sub> (g m <sup>-2</sup> d <sup>-1</sup> )	C <sub>night</sub> (g m <sup>-2</sup> night <sup>-1</sup> )	C <sub>net</sub> (g m <sup>-2</sup> 24 h <sup>-1</sup> )	Average salinity (psu)	Temp. (°C)	n
		Minimum	Maximum							
Russell Bank	March 16, 1999	2.705	2.837	12.0	0.423	0.213	0.636	31.6	21.6	6
Russell Bank	September 16, 1999	2.398	2.441	12.3	0.035	-0.025	0.010	41.8	29.9	6
Russell Bank	March 21, 2000	2.720	2.821	12.2	0.672	-0.061	0.611	23.5	27.5	6
Russell Bank	September 21, 2000	2.340	2.412	12.2	0.267	0.044	0.311	32.8	29.9	6
Barnes Key Bank	July 7, 2000	2.192	2.293	13.7	0.093	-0.007	0.086	37.6	32.0	6
Nine Mile Bank	October 2, 1998	2.248	2.275	*	*	*	2.206	34.8	30.4	5
Nine Mile Bank	March 12, 1999	2.475	2.562	*	*	*	*	33.4	24.3	3
Average (all banks)					0.432	0.211	0.643			

integrations. Nighttime rates (C<sub>night</sub>, g CaCO<sub>3</sub> m<sup>-2</sup> night<sup>-1</sup>) were determined by the difference.

## Results

### CALCIFICATION AND DISSOLUTION

C<sub>net</sub> on banks ranged from 0.010 to 2.206 g CaCO<sub>3</sub> m<sup>-2</sup> 24 h<sup>-1</sup>, with an average of 0.643 g CaCO<sub>3</sub> m<sup>-2</sup> 24 h<sup>-1</sup> (Table 2). Subaerial exposure of Nine Mile Bank during low tide prevented collection of continuous 24-h data sets at this location. Results for Nine Mile Bank listed in Table 2 represent approximately 13.5 h of data collection during day and night combined from two measurement attempts on October 2, 1998 and March 12, 1999. The average rate from this data set was extrapolated to 24 h. Highest rates of bank calcification (2.206 g CaCO<sub>3</sub> m<sup>-2</sup> 24 h<sup>-1</sup>) occurred on Nine Mile Bank located in the western region of Florida Bay. The lowest bank calcification rates occurred on Barnes Key Bank and Russell Bank (0.086 and 0.010 g CaCO<sub>3</sub> m<sup>-2</sup> 24 h<sup>-1</sup>, respectively) located in central Florida Bay.

Seasonal measurements were made on Russell Bank during winter (dry, cool) and summer (warm, wet) months from March 1999 to September 2000. The average C<sub>net</sub> on Russell Bank for all measurements is 0.392 g CaCO<sub>3</sub> m<sup>-2</sup> 24 h<sup>-1</sup>. Calcification rates on Russell Bank showed some seasonality with highest rates occurring during winter (March), and lowest rates occurring during summer (September; Table 2). The lowest calcification rates observed for banks were associated with hypersalinity events that we observed in central Florida Bay during September 1999 and July 2000. The hypersalinity event in September 1999 was concurrent with a high turbidity event. Hypersalinity events have been documented in Florida Bay during previous years (Fourqurean and Robblee 1999).

Rates of C<sub>net</sub> for intermediate density *Thalassia* beds ranged from 1.697 g CaCO<sub>3</sub> m<sup>-2</sup> 24 h<sup>-1</sup> to net dissolution of carbonate sediment (indicated by negative values) of -3.734 g CaCO<sub>3</sub> m<sup>-2</sup> 24 h<sup>-1</sup>

(Table 3). Buchanan Keys basin intermediate *Thalassia* beds (located in western Florida Bay) showed an average C<sub>net</sub> of 0.340 g CaCO<sub>3</sub> m<sup>-2</sup> 24 h<sup>-1</sup>, while Manatee Keys intermediate *Thalassia* beds (located in central Florida Bay) showed an average net dissolution rate of -0.510 g CaCO<sub>3</sub> m<sup>-2</sup> 24 h<sup>-1</sup>. The overall average for all intermediate *Thalassia* beds showed net dissolution of -0.230 g CaCO<sub>3</sub> m<sup>-2</sup> 24 h<sup>-1</sup>. The highest rate of dissolution observed for all data sets (-3.734 g CaCO<sub>3</sub> m<sup>-2</sup> 24 h<sup>-1</sup>) occurred in intermediate *Thalassia* beds near Manatee Keys and was associated with the September 1999 hypersalinity and high turbidity event that occurred in central Florida Bay.

Sparse *Thalassia* beds located near Captain Key and Manatee Keys, and mud bottom sites near Manatee Keys showed average rates of net carbonate sediment dissolution of -0.310 and -0.220 g CaCO<sub>3</sub> m<sup>-2</sup> 24 h<sup>-1</sup>, respectively (Table 3). C<sub>net</sub> for sparse *Thalassia* ranged from 0.497 g CaCO<sub>3</sub> m<sup>-2</sup> 24 h<sup>-1</sup> to dissolution of -0.899 g CaCO<sub>3</sub> m<sup>-2</sup> 24 h<sup>-1</sup>, while mud bottom rates ranged from 0.417 to dissolution of -0.979 g CaCO<sub>3</sub> m<sup>-2</sup> 24 h<sup>-1</sup>. While several attempts were made to collect hard bottom data in Buchanan Keys basin, only one complete 24-h data set was acquired in March 2000 due to difficulties in maintaining anchorage of the incubation chamber's support vessel on the hard substrate. Buchanan Keys basin hard bottom showed the highest C<sub>net</sub> measured for basins of 2.127 g CaCO<sub>3</sub> m<sup>-2</sup> 24 h<sup>-1</sup>.

### DIURNAL TRENDS

Twenty-two of 27 data sets showed diurnal cycles of calcification with the highest rates of net calcification (or lowest rates of net dissolution) occurring during daylight (C<sub>day</sub> ranged from 2.900 to -0.410 g CaCO<sub>3</sub> m<sup>-2</sup> d<sup>-1</sup>) and lowest rates of calcification (or highest rates of net dissolution) occurring during the night (C<sub>night</sub> ranged from 0.210 to -1.900 g CaCO<sub>3</sub> m<sup>-2</sup> night<sup>-1</sup>; Tables 2 and 3). Of the five complete bank calcification data sets collected, two (from Russell Bank) showed net

TABLE 3. Net calcification rates of representative substrate types in basins of Florida Bay.

Substrate description	Date	Total alkalinity (mmol kg <sup>-1</sup> )		Hours of sunlight	C <sub>day</sub> (g m <sup>-2</sup> d <sup>-1</sup> )	C <sub>night</sub> (g m <sup>-2</sup> night <sup>-1</sup> )	C <sub>24hr</sub> (g m <sup>-2</sup> 24 h <sup>-1</sup> )	Salinity (psu)	Temp (°C)	n
		Minimum	Maximum							
Intermediate <i>Thalassia</i>										
Manatee Keys	March 17, 1999	2.807	3.019	12.0	0.281	-1.197	-0.916	31.8	23.3	5
Manatee Keys	September 17, 1999	2.355	2.520	12.3	-2.218	-1.516	-3.734	41.8	30.0	8
Manatee Keys	March 23, 2000	2.735	2.818	12.2	0.839	-0.984	-0.145	25.4	25.9	7
Manatee Keys	March 24, 2000	2.693	2.765	12.3	1.559	-0.456	1.104	24.6	25.1	7
Manatee Keys	September 23, 2000	2.304	2.370	12.1	2.282	-1.320	0.962	36.6	30.0	6
Manatee Keys	September 23, 2000	2.288	2.374	12.1	1.623	-1.972	-0.349	36.6	30.0	6
Buchanon Keys	March 14, 1999	2.643	2.776	12.0	-0.411	-0.734	-1.145	34.9	24.5	6
Buchanon Keys	September 19, 1999	2.389	2.542	12.2	2.930	-1.233	1.697	36.1	28.6	6
Buchanon Keys	March 28, 2000	2.461	2.651	12.3	1.726	-1.268	0.458	33.8	26.0	7
Average					0.957	-1.187	-0.230			
Sparse <i>Thalassia</i>										
Captain Key	March 20, 2001	2.819	2.875	12.1	-0.539	-0.319	-0.858	35.0	28.3	6
Captain Key	March 21, 2001	2.874	2.905	12.1	-0.025	-0.378	-0.403	35.0	23.9	6
Captain Key	March 22, 2001	2.836	2.913	12.1	0.680	-0.183	0.497	35.0	22.4	6
Captain Key	March 23, 2001	2.869	2.895	12.1	0.107	-0.124	-0.017	35.0	21.3	6
Manatee Keys	March 22, 2003	2.681	2.793	12.2	-0.017	-0.542	-0.560	31.2	28.6	6
Manatee Keys	March 22, 2003	2.694	2.813	12.2	-0.089	-0.810	-0.899	31.2	28.6	6
Manatee Keys	March 23, 2003	2.781	2.818	12.2	0.342	-0.241	0.101	31.2	28.6	6
Average					0.066	-0.371	-0.306			
Hard bottom										
Buchanon Keys	March 29, 2000	2.428	2.574	12.3	1.606	0.520	2.127	33.6	28.1	7
Mud bottom										
Manatee Keys	March 26, 2000	2.752	2.769	12.3	0.714	-0.297	0.417	25.5	25.1	6
Manatee Keys	September 25, 2000	2.310	2.339	12.1	0.152	-0.035	0.117	36.8	30.9	6
Manatee Keys	March 25, 2003	2.621	2.705	12.2	0.317	-0.363	-0.046	35.7	25.2	6
Manatee Keys	March 26, 2003	2.640	2.715	12.3	-0.784	-0.195	-0.979	35.5	24.9	6
Manatee Keys	March 27, 2003	2.674	2.761	12.3	-0.455	-0.127	-0.583	35.5	24.7	6
Average					-0.011	-0.204	-0.215			

calcification during both day and night (Fig. 2, Table 2). Average C<sub>day</sub>, C<sub>night</sub>, and C<sub>net</sub> for banks was 0.432 g CaCO<sub>3</sub> m<sup>-2</sup> d<sup>-1</sup>, 0.211 g CaCO<sub>3</sub> m<sup>-2</sup> night<sup>-1</sup>, and 0.643 g CaCO<sub>3</sub> m<sup>-2</sup> 24 h<sup>-1</sup>, respectively. Net carbonate sediment production (C<sub>net</sub>) was observed at all bank locations.

Diurnal cycles of calcification were observed for all substrate types from each location within the basins. Figure 3 shows examples of diurnal trends in calcification rates and the corresponding TA measurements inside the incubation chamber from which they were calculated. Net carbonate sediment dissolution was observed during the night for all basin sites except for hard bottom sites located in Buchanon Keys basin (Fig. 3, Table 3). Net carbonate sediment dissolution (C<sub>net</sub>) was observed at 56% of all intermediate *Thalassia* sites, 75% of all sparse *Thalassia* sites, and 60% of all mud bottom sites.

Of the 22 data sets exhibiting diurnal calcification trends, 18 data sets (81.8%) showed net calcification during the day and net dissolution of carbonate sediments during the night, while 4 data sets (18.2%) showed net dissolution during both day and night with the lowest rates of dissolution

occurring during the day and the highest dissolution rates occurring during the night. Three of the four data sets showing low dissolution during the day and higher dissolution rates during the night occurred on sparse *Thalassia* beds near Captain Key (March 21, 2001) and Manatee Keys (March 26 and 27, 2001) in central Florida Bay, and the remaining data set was collected on an intermediate *Thalassia* bed in Buchanon Keys basin (March 14, 1999). Four data sets (Manatee Keys intermediate *Thalassia* on September 17, 1999, Captains Key sparse *Thalassia* on March 20, 2001, and Manatee Key mud bottom on March 26 and 27, 2003) showed higher rates of dissolution during the day and lower rates of dissolution during the night. Seven out of eight of the data sets showing dissolution both during day and night were acquired on days of complete cloud cover. The remaining data set was collected on Manatee Keys intermediate *Thalassia* on September 17, 1999, during the hypersalinity event. Insufficient data were collected from Nine Mile Bank to establish diurnal cycles in rates of calcification.

During 8 incubation chamber deployments (3 on Manatee Keys intermediate *Thalassia*, 1 on Buchanon Keys basin intermediate *Thalassia*, and 4 on



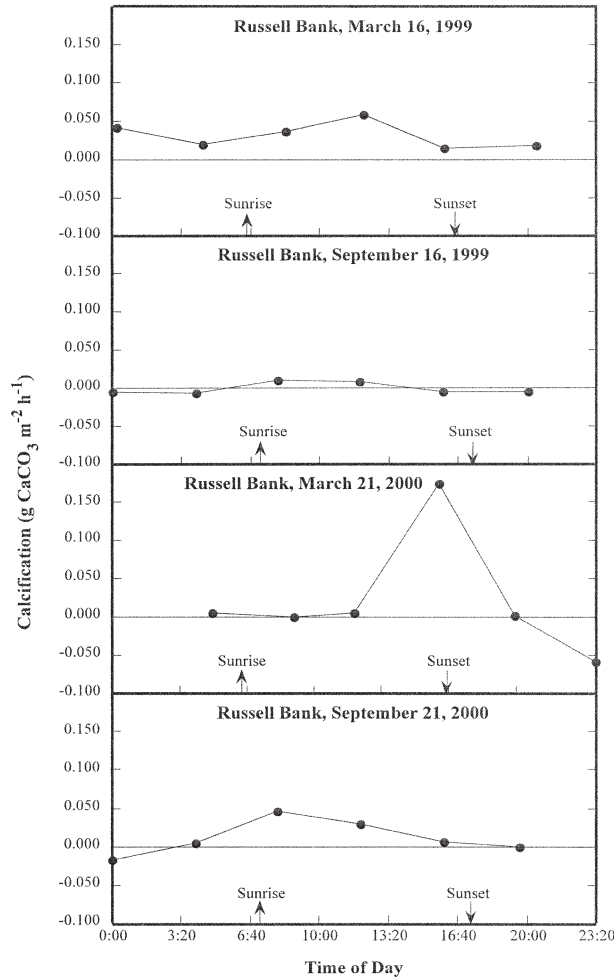


Fig. 2. Diurnal variation in rates of net calcification calculated from total alkalinity for mud banks in Florida Bay for March and September of 1999, and March and September of 2000. Positive values indicate net carbonate sediment production. Negative values indicate net carbonate sediment dissolution.

Manatee Keys mud bottom site), ambient TA was measured concurrently with incubation chamber measurements made every 4 h. These measurements were made to determine whether changes in incubation chamber TA ( $\Delta$ TA) reflect changes in the ambient environment. Ambient and chamber  $\Delta$ TA for Manatee Keys intermediate *Thalassia* on March 24, 2000, was 0.071 and 0.066 mmol kg<sup>-1</sup>, respectively (Fig. 4). Buchanan Keys basin intermediate *Thalassia* (March 28, 2000) showed an incubation chamber  $\Delta$ TA of 0.190 mmol kg<sup>-1</sup> and a  $\Delta$ TA in ambient water of 0.136 mmol kg<sup>-1</sup>. The  $\Delta$ TA for chamber and ambient water from Manatee Keys mud bottom site (March 26, 2003) was 0.044 and 0.056 mmol kg<sup>-1</sup>, respectively. Ambient TA measurements reflect diurnal cycles observed in incubation chamber measurements during calm sea states when wind-driven currents and mixing by

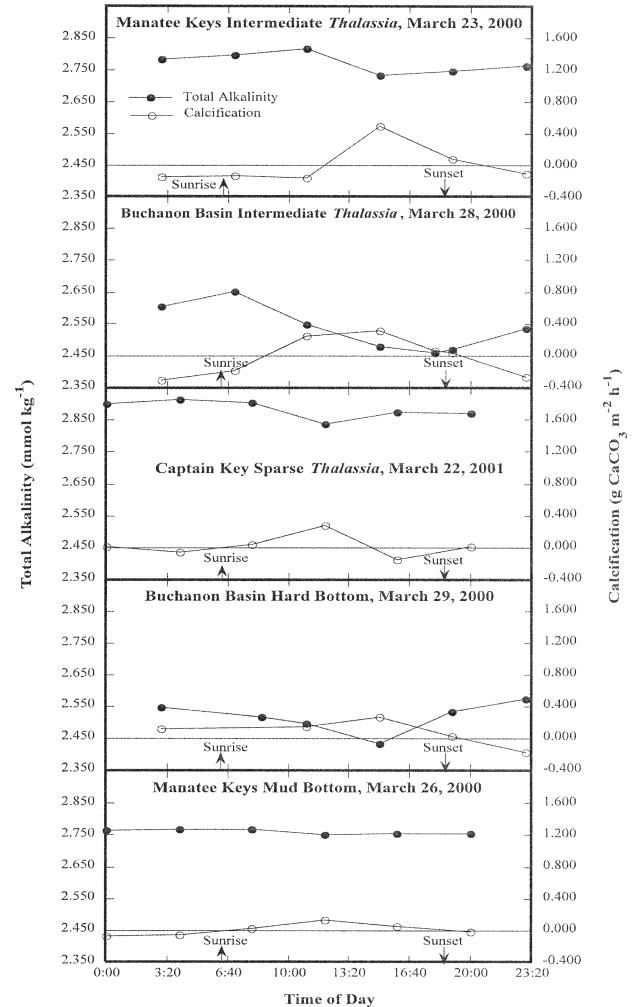


Fig. 3. Diurnal variation in rates of net calcification and corresponding total alkalinity measurements (inside of incubation chamber) for representative substrate types within basins of Florida Bay, including intermediate *Thalassia* seagrass beds near Manatee Keys and Buchanan Keys, sparse *Thalassia* seagrass beds near Captain Key, hard bottom near Buchanan Keys, and mud bottom near Manatee Keys. Positive values indicate net carbonate sediment production. Negative values indicate net carbonate sediment dissolution.

waves are at a minimum. TA decreases during daylight as calcification occurs and increases during the night when carbonate sediment dissolves. The average diurnal change in incubation chamber and ambient TA for the 8 concurrent data sets was 0.085 and 0.065 mmol kg<sup>-1</sup>, respectively. The average  $\Delta$ TA for all incubation chamber deployments and for ambient water on mud banks was 0.093 and 0.083 mmol kg<sup>-1</sup>, respectively. The agreement between chamber and ambient TA was less evident when ambient water was well mixed by strong currents and waves. Ambient TA on banks and in basins ranged from 2.192 to 2.837 and 2.277 to



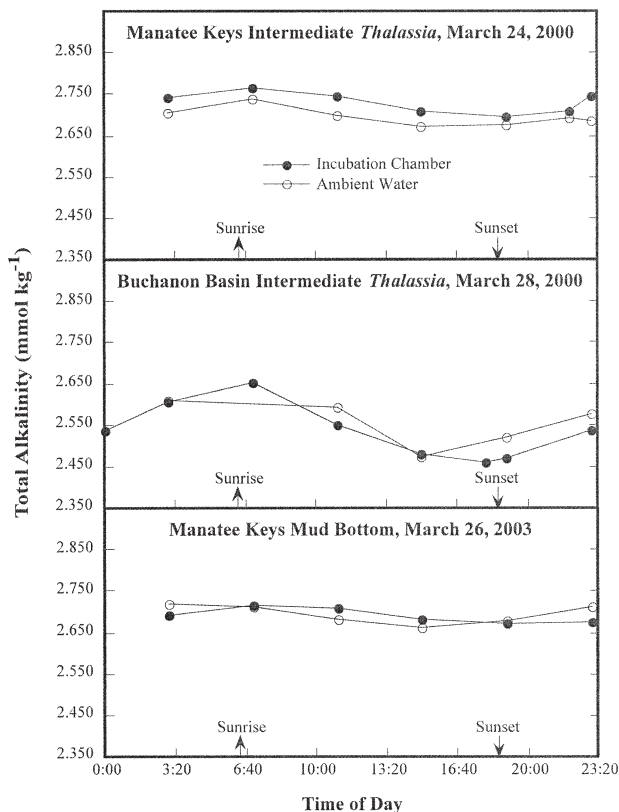


Fig. 4. Comparison of diurnal variation in total alkalinity inside of the incubation chamber and outside of the chamber in ambient water for representative basin sites including intermediate *Thalassia* seagrass beds near Manatee Keys and Buchanan Keys, and mud bottom near Manatee Keys.

2.711 mmol kg<sup>-1</sup>, respectively, while incubation chamber TA ranged from 2.192 to 3.019 mmol kg<sup>-1</sup> for all data sets. Ambient pH on banks and in basins ranged from 7.99 to 8.92 and 7.97 to 8.59, respectively, while pH in the incubation chamber ranged from 7.70 to 8.77 during all field expeditions. Comparison of diurnal trends in TA to DO and pH indicated that  $\Delta$ TA was inversely related to diurnal changes in pH and DO (Fig. 5). TA increased while DO and pH decreased during the night, and TA decreased while DO and pH increased during the day.

#### CORRELATIONS WITH TEMPERATURE AND SALINITY

Seasonal calcification data sets collected for mud banks and Manatee Keys intermediate *Thalassia* beds were used to correlate net calcification rates to salinity and temperature (Fig. 6). Mud bank calcification rates showed a negative correlation with both increasing salinity and temperature, with correlation coefficients ( $r^2$ ) of 0.78 and 0.64, respectively. A moderate negative correlation ( $r^2$  of 0.41) existed between Manatee Keys intermediate

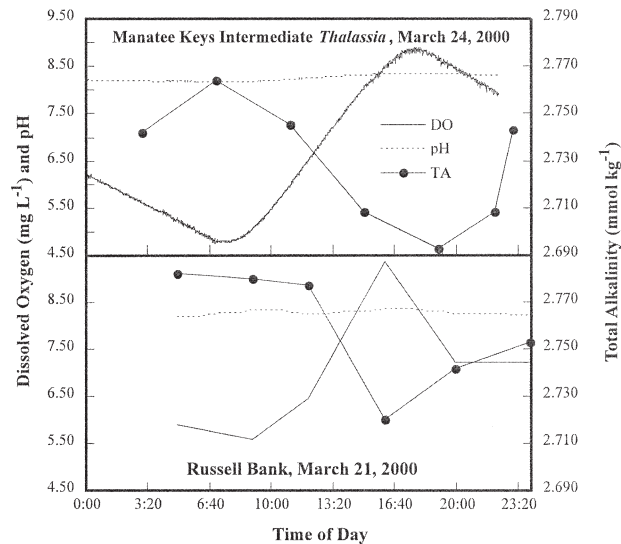


Fig. 5. Diurnal trends in dissolved oxygen (DO), pH, and total alkalinity (TA) for representative basin and mud bank study sites.

*Thalassia* calcification rates and salinity, and very little correlation ( $r^2$  of 0.07) existed between calcification rates and temperature.

## Discussion

### DIURNAL TRENDS

Our study is the first to quantify diurnal variation in community-level calcification rates in Florida Bay. Over 24-h time periods,  $\Delta$ TA (from which we calculated rates of calcification) ranged from 0.026 to 0.212 mmol kg<sup>-1</sup> for all data sets. Millero et al. (2001) and Boyer et al. (1999) reported seasonal nitrite, nitrate, and total phosphate concentrations for Florida Bay ranging from approximately 0 to 4.4  $\mu$ mol kg<sup>-1</sup> with the lowest concentrations occurring in central and western Florida Bay. Average diurnal  $\Delta$ TA of 0.098 mmol kg<sup>-1</sup> (or 98  $\mu$ mol kg<sup>-1</sup>) observed in our study is 22 times greater than total maximum nutrient concentrations. Salinity did not vary within the incubation chamber during collection of individual 24-h data sets in basins, so it is unlikely that diurnal  $\Delta$ TA at our basin study sites resulted from variation in nutrient concentrations or salinity, and can be attributed to carbonate sediment production and dissolution.

Based on calculations of TA with varying salinity performed using the carbonate speciation program CO2SYS (Lewis and Wallace 1998), we estimate that TA changes by 0.006 mmol kg<sup>-1</sup> for every one unit of salinity change. TA calculations were made over a salinity range of 25.0 to 41.2 in CO2SYS using dissociation constants K1 and K2 from Merbach et al. (1973) refit by Dickson and Millero (1987), KSO<sub>4</sub> from Dickson (1990), TCO<sub>2</sub> of 1.907 mmol kg<sup>-1</sup>,

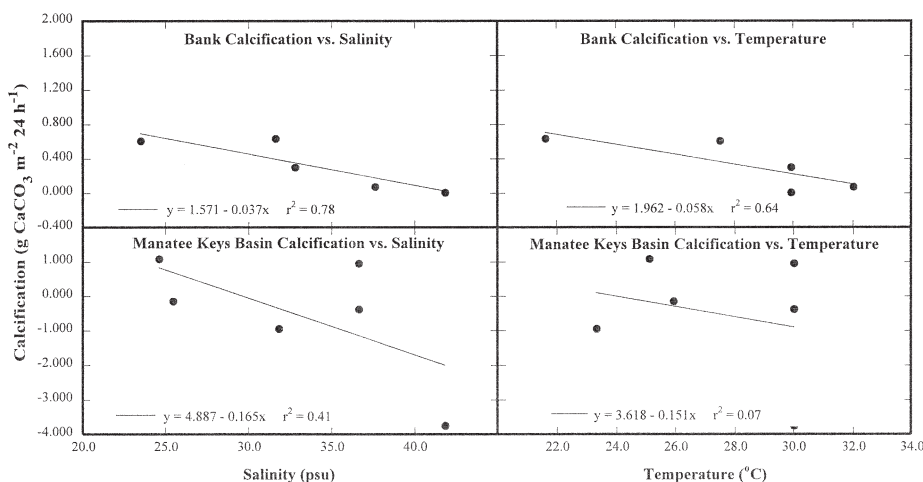


Fig. 6. Relation between net calcification ( $C_{\text{net}}$ ) and salinity, and  $C_{\text{net}}$  and temperature for seasonal mud bank measurements on Russell Bank and Barnes Key Bank and for basin measurements near Manatee Keys. Positive values indicate net carbonate sediment production. Negative values indicate net carbonate sediment dissolution.  $R$  is the correlation coefficient. The linear regression equation is in the form  $y = b + mx$ .

and a pH of 8.044 on the free hydrogen ion scale. We collected 41 sets of upstream and downstream TA measurements at 4-h intervals along transects across the tops of mud banks. Thirty-four (83%) of these 41 data sets showed a very small change in salinity ( $\Delta S$ ) from the upstream to downstream site of less than 1.0 (average  $\Delta S = 0.2$ , equivalent to a  $\Delta TA$  of  $0.001 \text{ mmol kg}^{-1}$ ) and an average  $\Delta TA$  from upstream to downstream sites of  $0.021 \text{ mmol kg}^{-1}$ . For these 34 data sets, approximately 5% of the  $\Delta TA$  may be attributed to variation in salinity. Four (10%) of the 41 data sets showed a salinity change from the upstream to downstream sampling sites of between 1.0 and 2.0 (average  $\Delta S = 1.5$ , equivalent to a  $\Delta TA$  of  $0.009 \text{ mmol kg}^{-1}$ ) and an average  $\Delta TA$  from upstream to downstream sites of  $0.024 \text{ mmol kg}^{-1}$  indicating that approximately 38% of the  $\Delta TA$  may be attributed to salinity variation in these data sets. The remaining three data sets (7%) showed a  $\Delta S$  from upstream to downstream of between 2.0 and 4.0 (average  $\Delta S = 3.3$ , equivalent to a  $\Delta TA$  of  $0.020 \text{ mmol kg}^{-1}$ ) and an average  $\Delta TA$  of  $0.031 \text{ mmol kg}^{-1}$  indicating that approximately 65% of the  $\Delta TA$  may be attributed to salinity variation in these data sets. We are confident that 95% of the  $\Delta TA$  in 83% of our mud bank data sets can be attributed to carbonate sediment production and dissolution, while 38–65% of the  $\Delta TA$  in the remaining 17% of mud bank data sets may be due to salinity variation.

TA measurements in our study (Tables 2 and 3) are within the range of previously measured Bay-wide TA (Millero et al. 2001). Lowest TA values were consistently observed during summer months, while highest values were observed during winter months.

This is consistent with seasonal trends in TA observed by Millero et al. (2001) and may be related to seasonal changes in evaporation and freshwater flow from the Everglades into Florida Bay. Although winter is the dry season, salinity tends to be lower than in summer because of lower evaporation rates (Nuttle et al. 2000; Swart and Price 2002), and TA is higher as more freshwater (characterized by high TA) is retained in Florida Bay (Millero et al. 2001). Millero et al. (2001) measured changes in salinity-normalized TA ( $\Delta NTA$ ), representative of seasonal changes in precipitation and dissolution of  $\text{CaCO}_3$ , for March and October 1998 ranging from approximately  $4.600$  to  $2.800 \text{ mmol kg}^{-1}$  ( $\Delta NTA = 1.800$ ) for central Florida Bay near Manatee Keys and from  $3.000$  to  $2.600 \text{ mmol kg}^{-1}$  ( $\Delta NTA = 0.400$ ) for western Florida Bay near Buchanan Keys. Our observed maximum diurnal  $\Delta TA$  at constant salinity near Manatee Keys ( $\Delta TA = 0.212$ ) and in Buchanan Basin ( $\Delta TA 0.190$ ) is approximately 12% and 48% of the seasonal variability observed in NTA reported for these areas from March to October 1998. The significant magnitude of diurnal  $\Delta TA$  suggests that the time of day must be carefully considered when comparing spatial or temporal TA data.

Diurnal trends in TA, DO, and pH (Fig. 5) are most notable for basin sites measured inside of the incubation chamber because bank measurements are complicated by changing current directions. Diurnal changes in DO typically reflect changes in  $\text{CO}_2$  resulting from photosynthesis as  $\text{O}_2$  is generated and  $\text{CO}_2$  is consumed, and respiration as  $\text{O}_2$  is consumed and  $\text{CO}_2$  is generated. This relation between TA, DO, and pH suggests that diurnal

calcification and dissolution trends are related to diurnal cycling of  $\text{CO}_2$  resulting from photosynthesis and respiration. Photosynthesis during the day facilitates calcification by photosynthetic organisms and consumes  $\text{CO}_2$ , reducing production of carbonic acid and dissolution of sediments. Aerobic respiration during the night generates  $\text{CO}_2$  (and carbonic acid), facilitating dissolution that, in some cases, exceeds nighttime calcification by calcifying organisms that are not dependent on light (e.g., mollusks). Photosynthesis is typically attenuated or inhibited during complete cloud cover and turbidity events. Our observation that dissolution occurred during daylight characterized by complete cloud cover or high levels of turbidity supports the link between diurnal calcification trends and diurnal cycling of  $\text{CO}_2$ .

#### CALCIFICATION

Previously reported annual rates of biogenic  $\text{CaCO}_3$  production in Florida Bay have been determined primarily from standing crop surveys of calcifying organisms and their growth rates (Nelson and Ginsburg 1986; Bosence 1989a; Frankovich and Zieman 1994). Organisms contributing to carbonate sediment production include seagrass epiphytes, small *Porites* and *Siderastrea* corals (western Florida Bay), mollusks, foraminifera, calcareous green algae, and coralline algae. Annual rates of carbonate sediment production determined from standing crop and turnover methods reflect only gross production and do not account for sediment transport or dissolution.

Bosence (1989a) measured annual sediment production for basin and bank areas near upper Cross Bank (central Florida Bay) of 128 and 331  $\text{g CaCO}_3 \text{ m}^{-2} \text{ yr}^{-1}$ , respectively, and near Buchanan Keys (western Florida Bay) of 506 and 1,081  $\text{g CaCO}_3 \text{ m}^{-2} \text{ yr}^{-1}$ , respectively, using standing crop and turnover methods. Nelson and Ginsburg (1986) reported annual carbonate sediment production rates for *Thalassia* epiphytes (one of the primary sources of lime mud in Florida Bay) ranging from 30 to 303  $\text{g CaCO}_3 \text{ m}^{-2} \text{ yr}^{-1}$  in the Cross Bank area. Frankovich and Zieman (1994) reported minimum annual epiphyte production ranges for 7 sites within Florida Bay of 1.9–282.7  $\text{g CaCO}_3 \text{ m}^{-2} \text{ yr}^{-1}$ . These annual rates correspond to daily production rates of 0.35–0.91  $\text{g CaCO}_3 \text{ m}^{-2} \text{ d}^{-1}$  for basins and banks near upper Cross Bank, and 1.39 and 2.96  $\text{g CaCO}_3 \text{ m}^{-2} \text{ d}^{-1}$  near Buchanan Keys (Bosence 1989a), 0.082–0.83  $\text{g CaCO}_3 \text{ m}^{-2} \text{ d}^{-1}$  for *Thalassia* epiphytes near Cross Bank (Nelson and Ginsburg 1986), and 0.005–0.77  $\text{g CaCO}_3 \text{ m}^{-2} \text{ d}^{-1}$  from Frankovich and Zieman (1994). Our average  $C_{\text{day}}$  values (which exclude the effect of net dissolution we observed during the night) for banks and basins, excluding mud bottom sites, ranged from 0.066 to 1.606  $\text{g}$

$\text{CaCO}_3 \text{ m}^{-2} \text{ d}^{-1}$  (Tables 2 and 3). Our measurements fall within the range of daily gross calcification values calculated from previous investigations (Nelson and Ginsburg 1986; Bosence 1989a; Frankovich and Zieman 1994). Highest  $C_{\text{day}}$  and  $C_{\text{net}}$  rates were observed for bank and basin sites located in western Florida Bay. This observation is consistent with previous measurements (Nelson and Ginsburg 1986; Bosence 1989a) showing higher rates of sediment production for western Florida Bay banks and basins.

Bank calcification shows a strong negative correlation with both temperature and salinity; basin calcification shows a moderate correlation only with salinity (Fig. 6). Lowest rates of calcification for both banks and basins occurred on Russell and Barnes Key Banks and near Manatee Keys during hypersalinity events in September 1999 (42 psu) and July 2000 (37.6 psu). Millero et al. (2001) indicated from seasonal TA measurements that during high salinity events in western Florida Bay precipitation of  $\text{CaCO}_3$  occurs and may be caused by inorganic precipitation due to the mixing of sediments with high salinity waters. Zieman et al. (1999) demonstrated from long-term, seasonal seagrass productivity data that higher salinities lead to reduced production by *T. testudinum*. Walker and Woelkerling (1988) indicated that production of some seagrass epiphytes, such as coralline algae, show reduced production during hypersalinity events. Our measurements of reduced calcification during high salinity events suggest that biogenic calcification as opposed to inorganic precipitation was the dominant contributor to carbonate sediment production at our study sites. The negative correlation between salinity and calcification indicates high salinity stress affects both calcifying organisms and seagrass production. As rates of biogenic calcification decrease and seagrass productivity (and sequestration of  $\text{CO}_2$ ) decreases, rates of carbonate sediment dissolution can exceed gross carbonate sediment production. The strong correlation of bank calcification, but not basin calcification, with temperature suggests that elevated salinity, not temperature, exerts the most control on rates of calcification. During summer field expeditions, we have frequently observed that bank top temperatures are noticeably warmer than basin temperatures. The strong correlation between calcification and temperature on banks suggests evaporation primarily driven by elevated bank top temperatures may be the primary mechanism for elevation of salinity.

#### DISSOLUTION

We report significant rates of carbonate sediment dissolution during the night at all basin sites (except

hard bottom) and at 50% of all bank sites. Average  $C_{\text{net}}$  values ranging from  $-0.306$  to  $0.643 \text{ g CaCO}_3 \text{ m}^{-2} \text{ 24 h}^{-1}$  are significantly lower than previously reported rates of gross calcification calculated by standing crop and turnover methods (Nelson and Ginsburg 1986; Bosence 1989a; Frankovich and Zieman 1994). Nighttime dissolution rates ( $C_{\text{night}}$ ) ranged between 8% and 71% of daytime calcification rates ( $C_{\text{day}}$ ) on banks that showed net dissolution during the night ( $n = 3$ ).  $C_{\text{night}}$  on basin substrates generally ranged between 23% and 122% of  $C_{\text{day}}$  at sites characterized by calcification during the day and dissolution at night ( $n = 13$ ). Eight locations measured during complete cloud cover were characterized by dissolution during both day and night. One Manatee Keys intermediate *Thalassia* site (Table 2, March 17, 1999) measured during a high turbidity event showed a nighttime dissolution rate four times greater than the daytime calcification rate.

Walter and Burton (1990) characterized pore fluid chemistry of shallow carbonate sediments in Florida Bay near Captain Key, Cross Bank, and Crane Key. They reported rates of carbonate sediment dissolution ranging from  $370$  to  $710 \mu\text{mol cm}^{-2} \text{ yr}^{-1}$ , or approximately  $1.01$  to  $1.95 \text{ g CaCO}_3 \text{ m}^{-2} \text{ d}^{-1}$ . Walter et al. (1993) and Ku et al. (1999) confirmed carbonate sediment dissolution at these same sites at a rate of  $400 \mu\text{mol cm}^{-2} \text{ yr}^{-1}$ , or  $1.1 \text{ g CaCO}_3 \text{ m}^{-2} \text{ d}^{-1}$  and suggested that over half the gross carbonate sediment production is dissolved or recrystallized. They attributed sediment dissolution to a combination of oxic respiration and sulfate reduction that generates carbonic acid for dissolution. Subsequent sulfide oxidation also generates acid for dissolution and prevents buildup of carbonate alkalinity ( $\text{HCO}_3^-$ ). Walter and Burton (1990) demonstrated that island flank sediments are characterized by higher total  $\text{CO}_2$  ( $\text{TCO}_2$ ), higher excess  $\text{Ca}^{2+}$  from sediment dissolution, and more bioturbation than mud bank sediments. They suggested that a greater degree of burrowing and transport of labile organic matter and  $\text{O}_2$  into sediments along seagrass root systems facilitates organic matter decomposition, sulfide oxidation, and increased acid production for sediment dissolution.

Our measured rates of carbonate sediment dissolution observed primarily during night are similar to the range of values previously reported for porewater dissolution (Walter and Burton 1990; Walter et al. 1993; Ku et al. 1999). Basin sites, similar to island flank sites of Walter and Burton (1990), showed higher rates of dissolution ( $-0.035$  to  $-1.972 \text{ g CaCO}_3 \text{ m}^{-2} \text{ night}^{-1}$ ) than banks ( $-0.007$  to  $-0.061 \text{ g CaCO}_3 \text{ m}^{-2} \text{ night}^{-1}$ ). Within basin sites, seagrass sites showed higher rates of

dissolution ( $-0.371$  to  $-1.187 \text{ g CaCO}_3 \text{ m}^{-2} \text{ night}^{-1}$ ) than mud bottom sites ( $-0.204 \text{ g CaCO}_3 \text{ m}^{-2} \text{ night}^{-1}$ ). The similarity of our dissolution rates to previous work on porewater dissolution suggests that porewater dissolution may impart a chemical signature to surface waters. Corbett et al. (1999, 2000) suggest that groundwater may flow across the sediment water interface, effectively carrying a porewater signature to surface waters in Florida Bay. These studies remain controversial due to potential error associated with use of seepage meters to measure groundwater fluxes (Shinn et al. 2002). Our fluorescein dye injections showed no dilution of incubation chamber water and no leakage of significant amounts of groundwater (or pore water) into the chamber. Ku et al. (1999) suggested that the rate of oxygen supply to sediment pore water required to maintain high sediment dissolution rates facilitated by sulfide oxidation requires that pore waters in the upper 24 cm of sediment exchange with overlying seawater on the order of once per several weeks to months. Porewater advection rates, alone, are too slow to account for the magnitude of our observed changes in surface water chemistry over 24-h periods. It is likely that changes in TA measured in surface water reflect the combined effect of sediment dissolution processes resulting from porewater reactions, biogenic calcification driven by diurnal cycling of  $\text{CO}_2$  through photosynthesis and respiration, and dissolution of surface sediments facilitated by elevated  $\text{pCO}_2$  from respiration during the night.

With the exception of hard bottom substrate, relative rates of dissolution increase with increasing seagrass cover from mud bottom to intermediate seagrass sites (Table 3). This trend may be due to a corresponding increase in respiring benthic faunal populations (e.g., molluscs, crustaceans) with increasing seagrass density resulting in higher rates of respiration that facilitate dissolution during the night and from enhanced diffusion of inorganic carbon species (from porewater sediment dissolution) along the root and burrow systems associated with seagrass beds (Walter and Burton 1990). Lower rates of dissolution on banks as compared to basins may be due to distribution of respiring versus photosynthetic calcifying species in addition to generally higher rates of calcification observed on banks due to larger numbers of calcifying epiphytes on bank seagrass (Bosence 1989a).

#### IMPLICATIONS FOR LONG-TERM SEDIMENT ACCUMULATION IN FLORIDA BAY

Stockman et al. (1967) provided the most widely accepted long-term estimates of sediment accumulation in Florida Bay based on thickness of sediment to bedrock in basins and on mud banks, and age of



sediment. This method accounts for carbonate sediment production, dissolution, and transport. They reported average accumulation rates of 5.3 cm 1000 yr<sup>-1</sup> for basins and 33 cm 1000 yr<sup>-1</sup> for banks. Weighting these two values to the relative proportion of total bank area in Florida Bay (10%) and basin area (90%; Stockman et al. 1967) yields an overall accumulation rate of 8 cm 1000 yr<sup>-1</sup>. This long-term average is much smaller than accumulation rates derived from short-term productivity measurements.

Measurement of biogenic CaCO<sub>3</sub> production rates by investigators using standing crop and turnover methods typically yields a broad range of sediment production rates, some of which are much greater than rates of accumulation. Bosence (1989a) presents the most comprehensive calculation of annual carbonate sediment production rates in Florida Bay banks and basins from standing crop surveys and short-term growth measurements of a number of carbonate sediment-producing organisms including *Porites*, *Thalassia* epiphytes, mollusks, *Penicillus*, Soritid foraminifera, and *Halimeda*. He reported annual sediment production rates for banks and basins in central Florida Bay (Cross Bank) of 331 and 128 g CaCO<sub>3</sub> m<sup>-2</sup> yr<sup>-1</sup>, respectively, and for banks and basins in western Florida Bay of 1,081 and 506 g CaCO<sub>3</sub> m<sup>-2</sup> yr<sup>-1</sup>, respectively. Conversion of these values to accumulation rates using a density of 2.8 g cm<sup>-3</sup> for CaCO<sub>3</sub> and 60% porosity (Stockman et al. 1967) results in bank and basin accumulation rates of 28.5 and 11 cm 1000 yr<sup>-1</sup>, respectively, for central Florida Bay, and 93 and 44 cm 1000 yr<sup>-1</sup> for western Florida Bay, respectively. Frankovich and Zieman (1994) estimated an overall accumulation rate of 7.2 cm 1000 yr<sup>-1</sup>. The difference between production and accumulation of sediments in both banks and basins has generally been attributed to transport of sediment out of the Bay, and transport of sediment from basins to banks within the Bay (Stockman et al. 1967; Bosence et al. 1985; Bosence 1989a,b; Prager and Halley 1999).

The method of measuring carbonate production used in our study, known as the alkalinity anomaly technique (Smith and Key 1975), provides a measure of net carbonate sediment production defined as gross carbonate production minus dissolution of carbonate sediments. Our measurements account for carbonate sediment production and dissolution but not sediment transport. This method differs from standing crop and turnover methods (e.g., Bosence 1989a) that provide a measure only of carbonate sediment produced, and from sediment thickness methods (e.g., Stockman et al. 1967) that account for carbonate sediment production, dissolution, and sediment transport over long time

periods (tens to thousands of years). Extrapolation of short-term productivity measurements to long-term sediment accumulation rates is highly speculative, and the associated error is difficult to quantify (Bosence 1989c; Frankovich and Zieman 1994). We present estimates of long-term sediment accumulation based on our short-term productivity measurements for comparison to other studies. We caution that these estimates are based on numerous assumptions and are likely to be accurate only to within an order of magnitude.

The basin substrate areas and total bank area used in our calculations were derived from Prager and Halley (1999), and include sparse seagrass, intermediate seagrass, hard bottom, mud bottom, dense seagrass, mixed bottom, open sand, and mud bottom suites. We have made the following assumptions with respect to substrate type. We collected no productivity data for open sand and have omitted it from our calculations. In our study areas, dense seagrass was located on top of banks and was included in mud bank measurements, so mud bank calcification rates were used to approximate dense seagrass values. The mixed bottom type of Prager and Halley (1999) represents a combination of the six other basin bottom type classifications and is estimated as the average of all other basin bottom type measurements included in our study. Our only hard bottom measurement is derived from western Florida Bay where hard bottom is generally characterized by the presence of coral, calcareous algae, and other calcifying organisms. Hard bottom sites in eastern and central Florida Bay contains fewer calcifying organisms, so our hard bottom accumulation estimate is likely to overestimate Bay-wide hard-bottom sediment production.

Average C<sub>net</sub> rates for each substrate type from Tables 2 and 3 were extrapolated to annual rates (Table 4). Sediment accumulation for each substrate type was calculated using methods of Stockman et al. (1967), a density for CaCO<sub>3</sub> of 2.8 g cm<sup>-3</sup>, and porosity (P) of 60%. Annual sediment production rates (g CaCO<sub>3</sub> m<sup>-2</sup> yr<sup>-1</sup>) were converted to sediment volume, SV (cm<sup>3</sup> m<sup>-2</sup> yr<sup>-1</sup>), using density for CaCO<sub>3</sub> (2.8 g cm<sup>-3</sup>) such that SV (cm<sup>3</sup> m<sup>-2</sup> yr<sup>-1</sup>) = production (g m<sup>-2</sup> yr<sup>-1</sup>) / density (2.8 g cm<sup>-3</sup>). The volume of sediment pore space (VPS) was determined using the equation  $P = VPS / (VPS + SV)$ . Addition of VPS and SV yielded the total volume of sediment and sediment pore space produced per year (cm<sup>3</sup> CaCO<sub>3</sub> m<sup>-2</sup> yr<sup>-1</sup>). This total volume (cm<sup>3</sup> m<sup>-2</sup> yr<sup>-1</sup>) was then converted to a sediment accumulation rate (cm 1000 yr<sup>-1</sup>) by multiplying by the conversion factor 1 m<sup>2</sup>/10000 cm<sup>2</sup> and time (1000 yr) such that accumulation rate (cm 1000 yr<sup>-1</sup>) =

TABLE 4. Long-term sediment accumulation rates for Florida Bay basins and mud banks. Substrate type, area, and % basin area data are from Prager and Halley (1999).  $C_{\text{net}}$  (average annual net calcification rate) is calculated from average  $C_{\text{net}}$  ( $\text{g CaCO}_3 \text{ m}^{-2}$ ) for each substrate type from Tables 1 and 2. Sediment accumulation is calculated as described in Stockman et al. (1967) for each substrate type. Weighted accumulation is the accumulation rate weighted to proportion of basin area. Combined accumulation is the sum of substrate-type components (sum of weighted accumulations) for basins and banks.

Substrate type	Area ( $\text{m}^2$ )	$C_{\text{net}}$ ( $\text{g CaCO}_3 \text{ m}^{-2} \text{ yr}^{-1}$ )	Sediment accumulation ( $\text{cm 1000 yr}^{-1}$ )	% total basin area	Weighted accumulation ( $\text{cm 1000 yr}^{-1}$ )	Combined accumulation ( $\text{cm 1000 yr}^{-1}$ )
Basins						19
Sparse seagrass	375,128,462	-112.0	-9.6	28	-2.7	
Intermediate seagrass	190,807,051	-83.9	-7.2	14	-1.0	
Hard bottom	439,668,144	776.0	66.9	33	22	
Mud bottom	209,804,241	-78.4	-6.8	16	-1.1	
Dense seagrass	65,288,753	235.0	20.2	5	1.0	
Mixed bottom	57,619,872	126.0	10.8	4	0.5	
Open sand	59,182,515	nd	nd	na	nd	
Banks						20
Mud bank suite	309,493,603	235.0	20.2	na	20	

total volume ( $\text{cm}^3 \text{ m}^{-2} \text{ yr}^{-1}$ )  $\times 1 \text{ m}^2 / 10000 \text{ cm}^2 \times$  time (1000 yr). Sediment accumulation for each basin type was weighted relative to the proportion of each basin substrate type per total area for basins in Florida Bay. Weighted sediment accumulation rates for all basin substrates were summed to derive a combined accumulation rate for basins.

Results of our long-term sediment accumulation calculations are shown in Table 4. We calculate average rates of long-term sediment accumulation in basins of  $19 \text{ cm 1000 yr}^{-1}$  and on banks of  $20 \text{ cm 1000 yr}^{-1}$ . Our basin value is higher than the Stockman et al. (1967) value of  $5.3 \text{ cm 1000 yr}^{-1}$ ; our bank value is lower than the Stockman et al. (1967) bank accumulation rate of  $33 \text{ cm 1000 yr}^{-1}$ . We assumed that enough sediment is transported to the banks from basins (Bosence 1989b,c; Bosence 1995) to generate the bank accumulation rate of  $33 \text{ cm 1000 yr}^{-1}$  measured by Stockman et al. (1967), and we corrected our basin and bank accumulation values for sediment transport, accordingly, by subtracting  $13 \text{ cm 1000 yr}^{-1}$  from our basin value of  $19 \text{ cm 1000 yr}^{-1}$ , and adding  $13 \text{ cm 1000 yr}^{-1}$  to our bank value of  $20 \text{ cm 1000 yr}^{-1}$ . Our corrected basin and bank accumulation values then become  $6 \text{ cm 1000 yr}^{-1}$  and  $33 \text{ cm 1000 yr}^{-1}$ , respectively. Weighting our basin and bank accumulation rates to the relative proportion of basins (90%) and banks (10%) as estimated by Stockman et al. (1967) gives an overall average rate of accumulation of  $8.7 \text{ cm 1000 yr}^{-1}$ . Interestingly, our sediment accumulation rate for basins (corrected for sediment transport only to banks) and our overall rate of accumulation are very similar to those of Stockman et al. (1967), suggesting that sediment dissolution may play a more important role than sediment transport out of the Bay as a cause for loss of carbonate sediment in Florida Bay.

## Conclusions

Our measurements of carbonate sediment production based on the alkalinity anomaly technique indicated consistent diurnal trends in calcification and sediment dissolution on mud banks and the various substrate types of which basins are comprised. Diurnal variation in surface water calcification and dissolution rates in Florida Bay is linked to cycling of  $\text{CO}_2$  in the water column through photosynthesis and respiration, as indicated by inverse correlations between TA and DO, and TA and pH. Seasonal measurements of carbonate sediment production on bank tops and in basins indicated an inverse correlation between sediment production and salinity. Highest rates of calcification occurred during winter months characterized by lower water temperatures, less surface water evaporation, and lower salinities.

Sediment dissolution rates were greatest during high salinity, turbidity, or cloud cover. These results suggest that an increase in the duration or frequency of seasonal hypersalinity events and high turbidity events may decrease the retention of carbonate sediments in Florida Bay due to elevated rates of dissolution. Additional monitoring of carbonate sediment production rates over a range of high salinity and high turbidity events is required to more accurately characterize and model the long-term impact of these stressors to carbonate sedimentation and the physical and chemical structure of Florida Bay.

Estimates of long-term sediment accumulation rates based on our short-term productivity measurements are very similar to estimates of Stockman et al. (1967) after correction of our data for sediment transport from basins to mud banks. Our short-term productivity measurements account for both sediment production and dissolution, whereas Stockman et al. (1967) account for sediment production, dissolution, and sediment transport both within the

bay and out of the bay. Thus, similarity between our estimates and those of Stockman et al. (1967) suggests that sediment dissolution in surface waters plays a more significant role than sediment transport in the loss of carbonate sediment from Florida Bay.

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